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TICT excited state of 4(1H-Pyrrol-1-yl) benzoic acid

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Abstract : Photoluminescence studies of 4(1H-Pyrrol-1-yl) benzoic acid (PBA) with general framework, donor and acceptor moieties connected through a single bond are presented Dual (local and CT) emission of PBA with a weak longer wavelength tail band has been observed for the first time The long wavelength anomalous band A has been assigned to fluorescence from TICT state

Keywords : Solvatochromic shift, fluorescence spectra, dipole moment

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1. Introduction

The idea of twisted intramolecular charge transfer state (TICT) [1] has given a boost for the quest of new tailor-made molecules to be used as fluorescent dyes [2], sensing of free volume in polymers [3], fluorescence pH or ion indicators [4], fluorescence solar collectors [5] and electron transfer photochemistry [6]. A suitable donor-acceptor moieties linked through the single bond or in rare cases double bond are good model of TICT molecules. TICT mechanism is an adiabatic photochemical reaction in excited state, which explains the abnormal dual fluorescence satisfactorily.

This is a preliminary report of the results of investigation of properties of 4(1H-pyrrol-1-yl) benzoic acid (PBA) in different solvents and temperatures.

2. Experimental

PBA was purchased from Aldrich Chemical Co (USA) and was sublimated under reduced pressure before use. All purified solvents were tested for any fluorescence in the wavelength region of interest. The absorption spectra at room temperature were recorded with a Shimadzu absorption spectrophotometer model UV-2101 PC and fluorescence and

phosphorescence spectra were obtained with a Perkin Elmer MPF-44A Spectrophotometer with low temperature attachment.

3. Result and Discussion

The hyposochromic shift of broad absorption band of PBA could be seen in the range of (34.36 – 35.71) × 10^3 cm^{-1} (Table 1) on going from nonpolar to polar solvent (aprotic to protic). This arises due to greater decrease in ground state energy in more polar solvent and hydrogen bonding solvent than excited state indicating an n, π^* transition [7].

Table 1. Absorption and emission data of PBA at 300 K and 77 K

Solvent	Absorption		Fluorescence			Phosphorescence		
	$\nu_a \times 10^{-3}$ (cm^{-1})	$\varepsilon_{max} \times 10^{-3}$ (M)	$\nu_B \times 10^{-3}$ (cm^{-1})	$\nu_A \times 10^{-3}$ (cm^{-1})	$\nu_C \times 10^{-3}$ (cm^{-1})	$\nu_p \times 10^{-3}$ (cm^{-1})	ϕ_p	τ_p (sec)
MCH	34 36	–	29 85	-	–	24 69	0.20	2 30
CH	34 48		29 41	-	-	–	-	-
MeOH	35 58	–	30 30	23 25	17 54	25 00	0 28	2 12
EtOH	35 71	8 7	29.41	24 39	17 54	25 30	0 30	2 11
1-ButOH	34 96	8 4	29 14	21 97	17 54	–	–	–
ACN	35 08	8 7	29 14	20 83	17 85		–	–
$CHCl_3$	34 36	9 2	30 30	23 80	17 54	-	–	–
N,N-DMF	35 33	10 3	30 30	22.22	17 69	-	–	–

a-absorption, B-first fluorescence band, A-second fluorescence band, C-third fluorescence band,

Figure 1 exhibits prominent dual fluorescence peaks with another longer wavelength weak tail band in different polar solvents and only one band (*i.e.* normal band B) in nonpolar solvent at 300 K. In both types of solvents, the normal band B appears at around

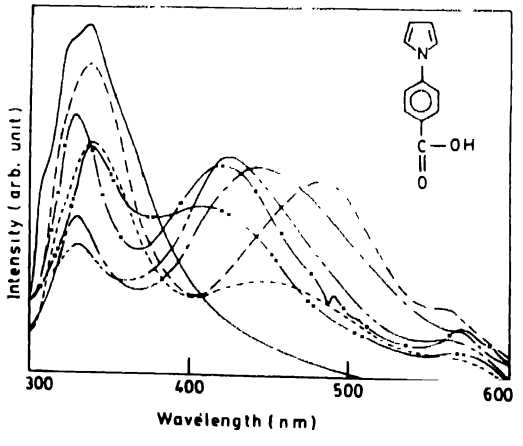

Figure 1. Fluorescence spectra of PBA in various solvents. (——) CH, (– – –) ACN; (– • –) N,N—DMF. (—• •—) MeOH, (—— • ——) $CHCl_3$; (—• • •—) EtOH; (-----) 1-ButOH.

29.41 × 10^3 cm^{-1} region. But quantum yield of band B is ten times greater in nonpolar media. Origin of this band may be attributed to $^1B_{2u} \rightarrow {}^1A_{1g}$ transition of benzene. Now the broad structureless anomalous band A appears at lower energy region producing large bathochromic shift with solvent polarity (Table 1). This polarity effect of band A points to have a large dipole moment in excited state. The computed dipole moment change or $\Delta\mu$ [8] between ground and excited state ($\mu_e - \mu_g$) was found to be 32 Debye. This large value of dipole moment indicates that band A has a polar character or intramolecular charge transfer state [9].

Figure 2 shows the temperature dependence of the two bands in acetonitrile solvent in the temperature range of 283 K – 338 K. The intensity of the normal band B decreases as usual with increasing temperature while the intensity of other band A increases. This behaviour points that the emitting charge transfer (CT) state may be TICT state [7]. Further we see at 77 K in glass matrices, PBA shows only normal fluorescence

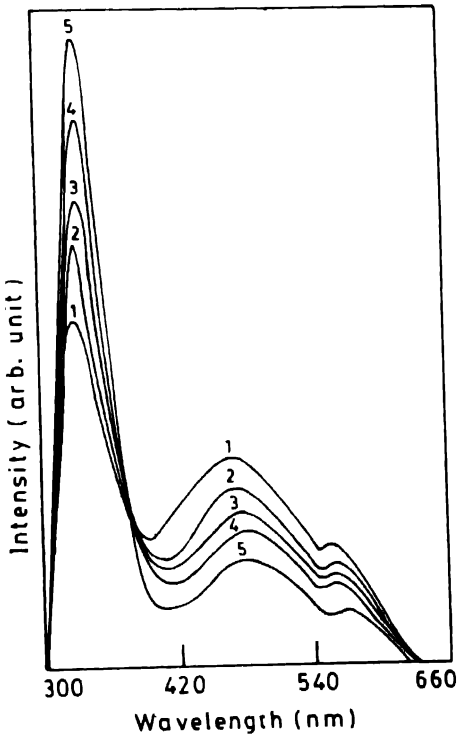

Figure 2. Fluorescence spectra of PBA in acetonitrile at various temperature.
(1) 338K; (2) 323K; (3) 313K; (4) 303K; (5) 293K.

band in both polar and nonpolar solvents with nearly equal quantum yield ($\phi_f = 0.3$); and in addition to this, it shows a strong phosphorescence band in the wavelength region of band A. We assign this triplet state to be n,π^* in nature, from the blue shift of 0,0 band by polarity effect, although the lifetime of this phosphorescence is quite larger than expected value.

The third weak band of the fluorescence spectra appear in polar solvent at (17.24 – 17.45) × 10^3 cm^{-1} region. This tail band of the fluorescence spectra vanishes with increase of concentration. This band makes its appearance at the concentration range of (10^{-5} – 10^{-6}) M/L. Above and below this concentration, this band reduced to nothing. Another interesting feature of this band is that, at different higher temperatures, its intensity is increased corresponding to TICT band, keeping the intensity ratio constant. At low temperature, like band A, it also vanishes.

The absence of band A in rigid matrices, the presence of this band in polar media and intensity enhancement of this band at higher temperature, confirmed that this corresponds to TICT state. So in PBA, TICT state may have formed through the rotation of pyrrol ring about single bond connected with benzoic acid. Furthermore, we can conclude from the concentration effect of tail band that there might also some 'in vitro' cases where TICT reaction is combined either in series or in parallel [10] with other adiabatic photoreactions such as intra or inter-molecular excimer or exciplex formation.

Detailed work on this is in progress and the results of which may be subject of a future paper

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